CHAPTER 15

Chemical Equilibrium

"Old chemists never die, they just reach equilibrium."

Anonymous

15.1 Life: Controlled Disequilibrium

Dynamic equilibrium involves two opposing processes occurring at the same rate. This image draws an analogy between a chemical equilibrium ($N_2O_4 \rightleftharpoons 2\ NO_2$) in which the two opposing reactions occur at the same rate and a freeway with traffic moving in opposing directions at the same rate.

Have you ever tried to define life? If you have, you know that defining life is difficult. How are living things different from nonliving things? You may try to define living things as those things that can move. But of course many living things do not move—many plants, for example, do not move very much—and some nonliving things, such as glaciers and Earth itself, do move. So motion is neither unique to nor definitive of life. You may try to define living things as those things that can reproduce. But again, many living things, such as mules or sterile humans, cannot reproduce; yet they are alive. In addition, some nonliving things—such as crystals, for example—reproduce (in some sense). So what is unique about living things?

One definition of life uses the concept of equilibrium. We will define *chemical* equilibrium more carefully soon. For now, we can think more generally of equilibrium as *sameness and constancy*. When an object is in equilibrium with its surroundings, some property of the object has reached sameness with the surroundings and is no longer changing. For example, a cup of hot water is not in equilibrium with its surroundings with respect to temperature. If left undisturbed, the cup of hot water will slowly cool until it reaches equilibrium with its surroundings. At that point, the temperature of the water is the *same as* that of the surroundings (sameness) and *no longer changes* (constancy).

So equilibrium involves sameness and constancy. Part of a definition for living things, then, is that living things *are not* in equilibrium with their surroundings. Our body temperature, for example, is not the same as the temperature of our surroundings. When we jump into a swimming pool, the pH of our blood does not become the same as the pH of the surrounding water. Living things, even the simplest ones, maintain some measure of *disequilibrium* with their environment.

We must add one more concept, however, to complete our definition of life with respect to equilibrium. Our cup of hot water is in disequilibrium with its environment, yet it is not alive. However, the cup of hot water has no control over its disequilibrium and will slowly come to equilibrium with its environment. In contrast, living things—as long as they are alive—maintain and *control* their disequilibrium. Your body temperature, for example, is not only in disequilibrium with your surroundings—it is in controlled disequilibrium. Your body maintains your temperature within a specific range that is not in equilibrium with the surrounding temperature.

So one definition for life is that living things are in *controlled disequilibrium* with their environment. A living thing comes into equilibrium with its surroundings only after it dies. In this chapter, we will examine the concept of equilibrium, especially chemical equilibrium—the state that involves sameness and constancy.

15.2 The Rate of a Chemical Reaction

Reaction rates are related to chemical equilibrium because, as we will see in Section 15.3, a chemical system is at equilibrium when the rate of the forward reaction equals the rate of the reverse reaction.

A reaction rate can also be defined as the amount of a product that forms in a given period of time.

Before we probe more deeply into the concept of chemical equilibrium, we must first understand something about the rates of chemical reactions. The **rate of a chemical reaction** is the amount of reactant that changes to product in a given period of time. A reaction with a fast rate proceeds quickly, with a large amount of reactant being converted to product in a certain period of time (▶ Figure 15.1a). A reaction with a slow rate proceeds slowly, with only a small amount of reactant being converted to product in the same period of time (Figure 15.1b).

Chemists seek to control reaction rates for many chemical reactions. For example, the space shuttle is propelled by the reaction of hydrogen and oxygen to form water. If the reaction proceeds too slowly, the shuttle will not lift off the ground. If, however, the reaction proceeds too quickly, the shuttle can explode. Reaction rates can be controlled if we understand the factors that influence them.

Collision Theory

According to **collision theory**, chemical reactions occur through collisions between molecules or atoms. For example, consider the following gas phase chemical reaction between $H_2(g)$ and $I_2(g)$ to form $HI(g)$.

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$$

The reaction begins when an H_2 molecule collides with an I_2 molecule. If the collision occurs with enough energy—that is, if the colliding molecules are moving fast enough—the product molecules (HI) form. If the collision occurs without enough energy, the reactant molecules (H_2 and I_2) simply bounce off of one another. Since gas-phase molecules have a wide distribution of velocities, collisions occur with a wide distribution of energies. The high-energy collisions lead to products and the low-energy collisions do not.

Whether a collision leads to a reaction also depends on the *orientation* of the colliding molecules, but this topic is beyond our current scope.

The reason that higher-energy collisions are more likely to lead to products is related to a concept called the *activation energy* of a reaction.

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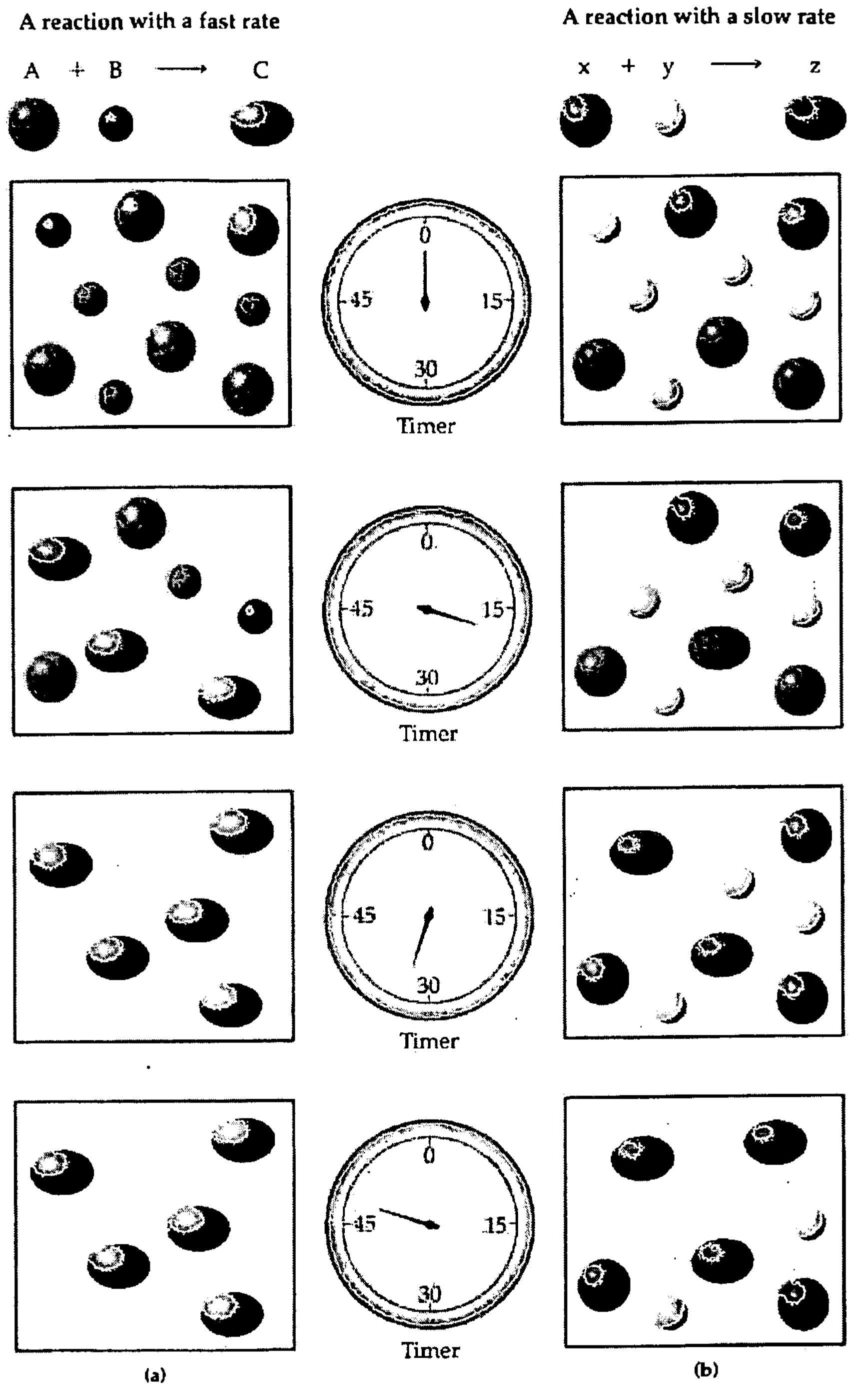
Figure 15.1 Reaction rates (a) In a reaction with a fast rate, the reactants react to form products in a short period of time. (b) In a reaction with a slow rate, the reactants react to form products over a long period of time.



The activation energy for chemical reactions is discussed in more detail in Section 15.12. For now, we can think of the activation energy as a barrier that must be overcome for the reaction to proceed. For example, in the case of H_2 reacting with I_2 to form HI, the product (HI) can begin to form only after the H–H bond and the I–I bond each begin to break. The activation energy is the energy required to begin to break these bonds.

If molecules react via high-energy collisions, what factors influence the rate of a reaction? What factors affect the number of high-energy collisions that occur per unit time? There are two important factors: the *concentration* of the reacting molecules and the *temperature* of the reaction mixture.

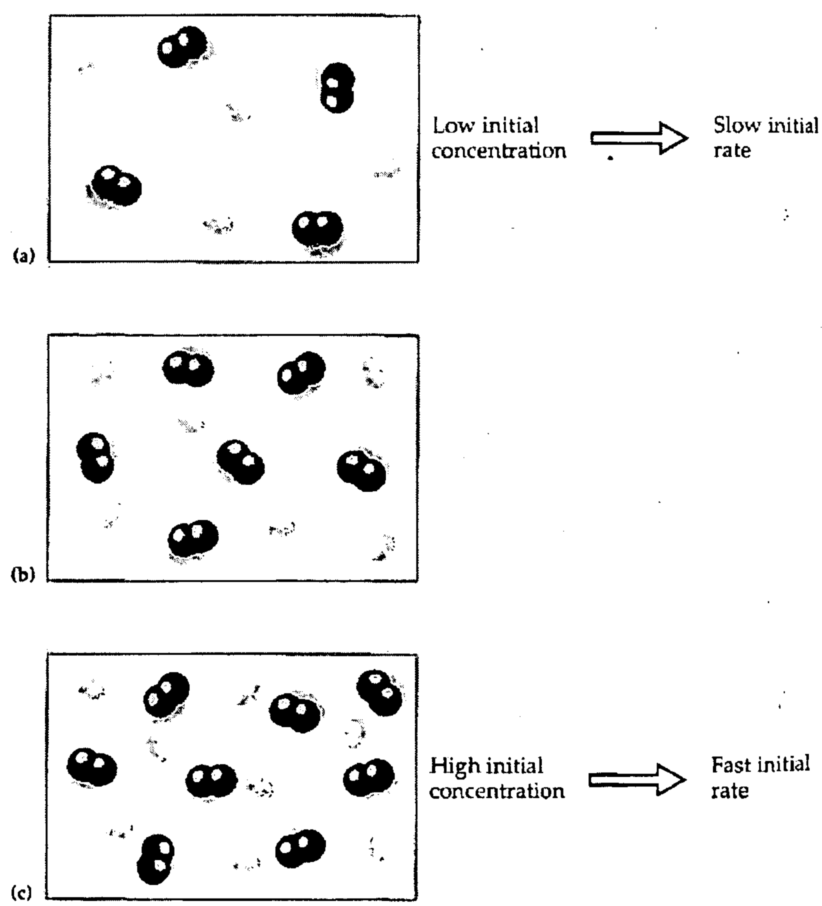
How Concentration Affects the Rate of a Reaction

▼ Figures 15.2a through c show various mixtures of H_2 and I_2 at the same temperature but different concentrations. If H_2 and I_2 react via collisions to form HI, which mixture do you think will have the highest reaction rate? Since Figure 15.2c has the highest concentration of H_2 and I_2, it will have the most collisions per unit time and therefore the fastest reaction rate. This idea holds true for most chemical reactions.

> The rate of a chemical reaction generally increases with increasing concentration of the reactants.

The exact relationship between increases in concentration and increases in reaction rate varies for different reactions and is beyond our current scope.

$H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$



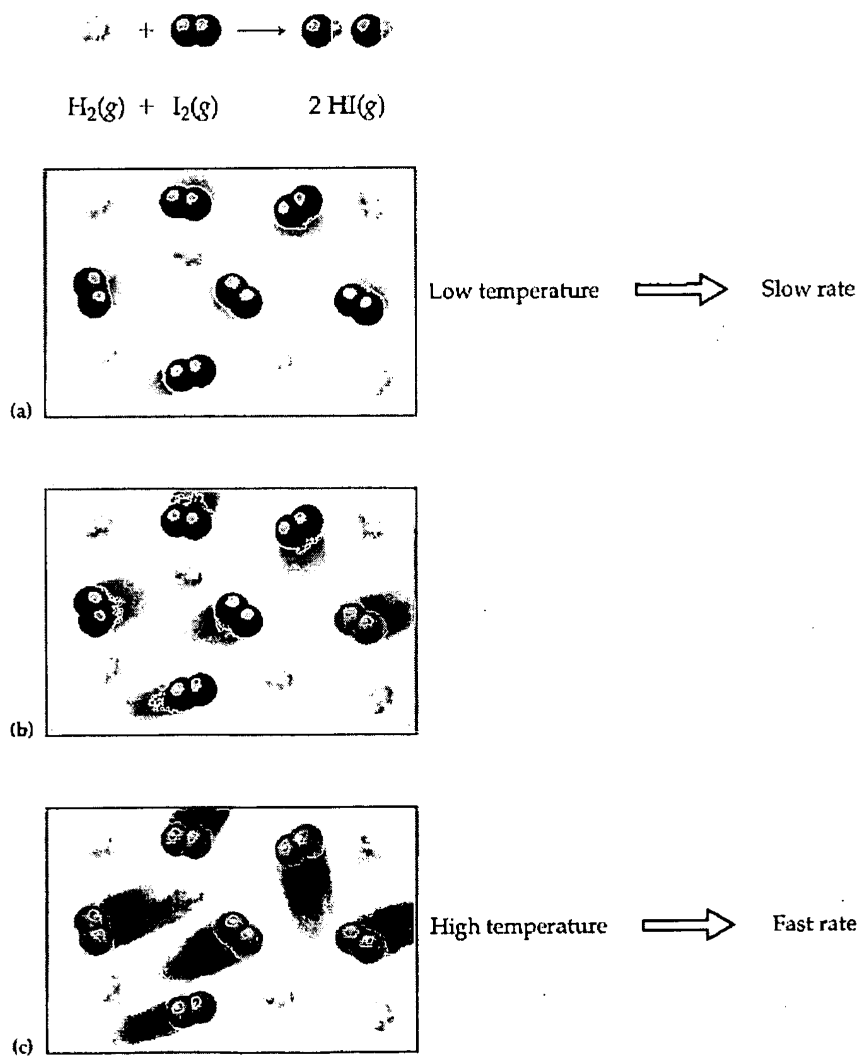
▲ **Figure 15.2 Effect of concentration on reaction rate** Question: Which reaction mixture will have the fastest initial rate? The mixture in (c) is fastest because it has the highest concentration of reactants and therefore the highest rate of collisions.

For our purposes, it will suffice to know that for most reactions the reaction rate increases with increasing reactant concentration.

Knowing this, what can we say about the rate of a reaction as the reaction proceeds? Since reactants turn to products in the course of a reaction, their concentration decreases. Consequently, the reaction rate decreases as well. In other words, as a reaction proceeds, there are fewer reactant molecules (because they have turned into products), and the reaction slows down.

How Temperature Affects the Rate of a Reaction

Reaction rates also depend on temperature. ▼ Figures 15.3a through c show various mixtures of H_2 and I_2 at the same concentration, but different temperatures. Which will have the fastest rate? Raising the temperature makes



▲ **Figure 15.3 Effect of temperature on reaction rate** Question Which reaction mixture will have the fastest initial rate? The mixture in (c) [illegible] because it has the highest temperature.

the molecules move faster (Section 3.9). They therefore experience more collisions per unit time, resulting in a faster reaction rate. In addition, higher temperature results in more collisions that are (on average) of higher energy. Since it is the high-energy collisions that result in products, this also produces a faster rate. Consequently, Figure 15.3c (which has the highest temperature) has the fastest reaction rate. This relationship holds true for most chemical reactions.

The rate of a chemical reaction generally increases with increasing temperature of the reaction mixture.

The temperature dependence of reaction rates is the reason that cold-blooded animals become more sluggish at lower temperatures. The reactions required for them to think and move simply become slower, resulting in the sluggish behavior.

To summarize:

- Reaction rates generally increase with increasing reactant concentration.
- Reaction rates generally increase with increasing temperature.
- Reaction rates generally decrease as a reaction proceeds.

✔ **CONCEPTUAL CHECKPOINT 15.1**

In a chemical reaction between two gases, you would expect that increasing the pressure would probably

(a) increase the reaction rate
(b) decrease the reaction rate
(c) not affect the reaction rate

15.3 The Idea of Dynamic Chemical Equilibrium

What would happen if our reaction between H_2 and I_2 to form HI were able to proceed in both the forward and reverse directions?

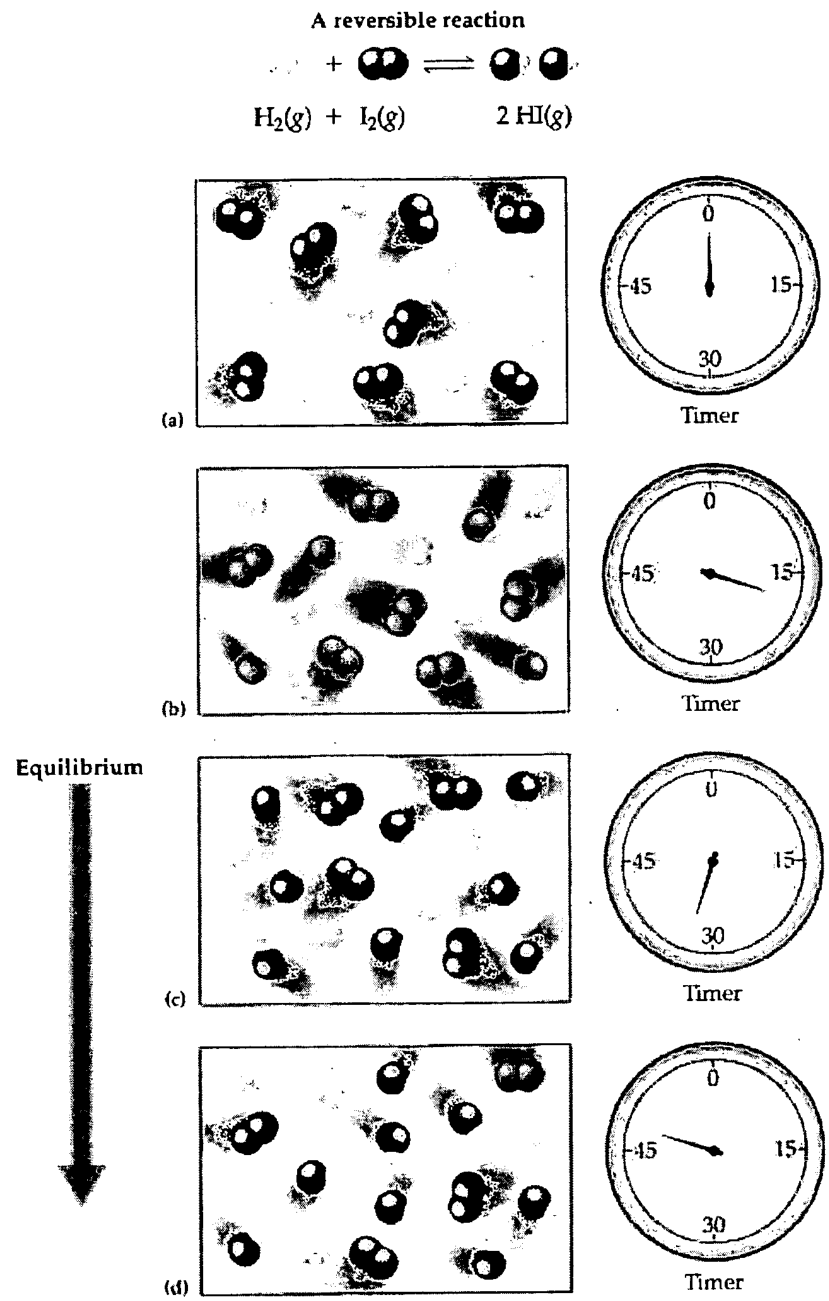
$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Now, H_2 and I_2 can collide and react to form 2 HI molecules, but the 2 HI molecules can also collide and react to reform H_2 and I_2. A reaction that can proceed in both the forward and reverse directions is said to be a **reversible reaction.**

Suppose we begin with only H_2 and I_2 in a container (▶ Figure 15.4a). What happens initially? H_2 and I_2 begin to react to form HI (Figure 15.4b). However, as H_2 and I_2 react their concentration decreases, which in turn decreases the rate of the forward reaction. At the same time, HI begins to form. As the concentration of HI increases, the reverse reaction begins to occur at an increasingly faster rate because there are more HI collisions. Eventually the rate of the reverse reaction (which is increasing) equals the rate of the forward reaction (which is decreasing). At that point, **dynamic equilibrium** is reached (Figures 15.4c and 15.4d).

Dynamic equilibrium—In a chemical reaction, the condition in which the rate of the forward reaction equals the rate of the reverse reaction.

This condition is not static—it is dynamic because the forward and reverse reactions are still occurring, but at a constant rate. When dynamic



▲ **Figure 15.4 Equilibrium** When the concentrations of the reactants and products no longer change, equilibrium has been reached.

equilibrium is reached, the concentrations of H_2, I_2, and HI no longer change. They remain the same because the reactants and products are being depleted at the same rate at which they are being formed.

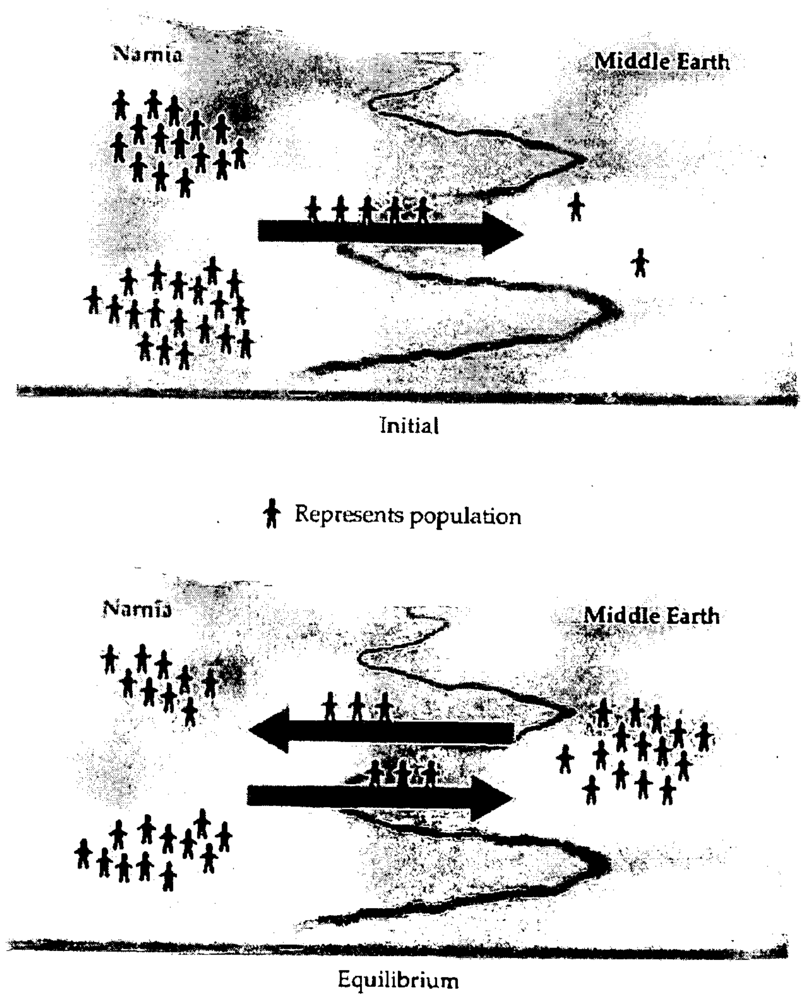
Notice that dynamic equilibrium includes the concepts of sameness and constancy that we discussed in Section 15.1. When dynamic equilibrium is reached, the forward reaction rate is the same as the reverse reaction rate (sameness). Because the reaction rates are the same, the concentrations of the reactants and products no longer change (constancy). However, just because

the concentrations of reactants and products no longer change at equilibrium does *not* imply that the concentrations of reactants and products are equal to one another at equilibrium. Some reactions reach equilibrium only after most of the reactants have formed products. (Recall strong acids from Chapter 14.) Others reach equilibrium when only a small fraction of the reactants have formed products. (Recall weak acids from Chapter 14.) It depends on the reaction.

We can better understand dynamic equilibrium with a simple analogy. Imagine that Narnia and Middle Earth are two neighboring kingdoms (▼Figure 15.5). Narnia is overpopulated and Middle Earth is underpopulated. One day, however, the border between the two kingdoms opens, and people immediately begin to leave Narnia for Middle Earth (call this the forward reaction).

$$\text{Narnia} \longrightarrow \text{Middle Earth} \quad \text{(forward reaction)}$$

The population of Narnia goes down as the population of Middle Earth goes up. As people leave Narnia, however, the *rate* at which they leave begins to slow down (because Narnia becomes less crowded). On the other hand, as



▲ Figure 15.5 **Population analogy for a chemical reaction proceeding to equilibrium**

people move into Middle Earth, some decide it was not for them and begin to move back (call this the reverse reaction).

$$\text{Narnia} \longleftarrow \text{Middle Earth} \quad \text{(reverse reaction)}$$

As Middle Earth fills, the rate of people moving back to Narnia gets faster. Eventually the *rate* of people moving out of Narnia (which has been slowing down as people leave) equals the *rate* of people moving back to Narnia (which has been increasing as Middle Earth gets more crowded). Dynamic equilibrium has been reached.

$$\text{Narnia} \rightleftharpoons \text{Middle Earth}$$

Notice that when the two kingdoms reach dynamic equilibrium, their populations no longer change because the number of people moving out equals the number of people moving in. However, one kingdom—because of its charm, the character of its leader, the availability of better jobs, a lower tax rate, or whatever other reason—may have a higher population than the other kingdom, even when dynamic equilibrium is reached.

Similarly, when a chemical reaction reaches dynamic equilibrium, the rate of the forward reaction (analogous to people moving out of Narnia) equals the rate of the reverse reaction (analogous to people moving back into Narnia), and the relative concentrations of reactants and products (analogous to the relative populations of the two kingdoms) become constant. Also, like our two kingdoms, the concentrations of reactants and products will not necessarily be equal at equilibrium, just as the populations of the two kingdoms are not equal at equilibrium.

15.4 The Equilibrium Constant: A Measure of How Far a Reaction Goes

We have just learned that the *concentrations* of reactants and products are not equal at equilibrium—it is the *rates* of the forward and reverse reactions that are equal. But what about the concentrations? What can we know about them? The equilibrium constant (K_{eq}) is a way to quantify the concentrations of the reactants and products at equilibrium. Consider the following generic chemical reaction

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$$

where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the respective stoichiometric coefficients in the chemical equation. The **equilibrium constant (K_{eq})** for the reaction is defined as the ratio—at equilibrium—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients.

$$K_{eq} = \frac{\overbrace{[\text{C}]^c[\text{D}]^d}^{\text{Products}}}{\underbrace{[\text{A}]^a[\text{B}]^b}_{\text{Reactants}}}$$

The equilibrium constant quantifies the relative concentrations of reactants and products at equilibrium.

Writing Equilibrium Expressions for Chemical Reactions

To write an equilibrium expression for a chemical reaction, simply examine the chemical equation and follow the preceding definition. For example, suppose we want to write an equilibrium expression for the following reaction.

$$2\,N_2O_5(g) \rightleftharpoons 4\,NO_2(g) + O_2(g)$$

The equilibrium constant is $[NO_2]$ raised to the fourth power multiplied by $[O_2]$ raised to the first power divided by $[N_2O_5]$ raised to the second power.

$$K_{eq} = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

Notice that the *coefficients* in the chemical equation become the *exponents* in the equilibrium expression.

$$2\,N_2O_5(g) \rightleftharpoons 4\,NO_2(g) + O_2(g)$$

Implied 1

$$K_{eq} = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

EXAMPLE 15.1 Writing Equilibrium Expressions for Chemical Reactions

Write an equilibrium expression for the following chemical equation.

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

The equilibrium expression is the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients. Notice that the expression is a ratio of products over reactants. Notice also that the coefficients in the chemical equation are the exponents in the equilibrium expression.

Solution:

$$K_{eq} = \frac{[CH_3OH]}{[CO][H_2]^2}$$

Product

Reactants

SKILLBUILDER 15.1 Writing Equilibrium Expressions for Chemical Reactions

Write an equilibrium expression for the following chemical equation.

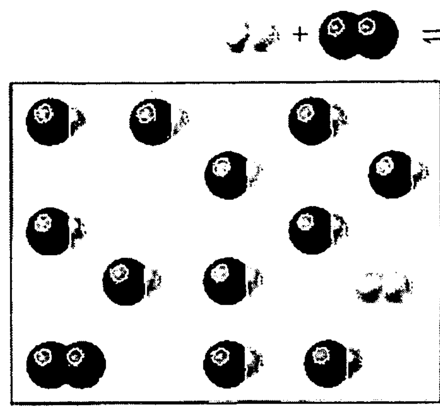
$$H_2(g) + F_2(g) \rightleftharpoons 2\,HF(g)$$

The Significance of the Equilibrium Constant

Given this definition of an equilibrium constant, what does it mean? What, for example, does a large equilibrium constant ($K_{eq} \gg 1$) imply about a reaction? It means that the forward reaction is largely favored and that there will be more products than reactants when equilibrium is reached. For example, consider the following reaction.

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g) \qquad K_{eq} = 1.9 \times 10^{19} \text{ at } 25\ ^\circ C$$

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$



$$K_{eq} = \frac{[HBr]^2}{[H_2][Br_2]} = \text{Large Number}$$

▲ **Figure 15.6 The meaning of a large equilibrium constant** A large equilibrium constant means that there will be a high concentration of products and a low concentration of reactants at equilibrium.

The equilibrium constant is large, meaning that at equilibrium the reaction lies far to the right—high concentrations of products, tiny concentrations of reactants (▲ Figure 15.6).

Conversely, what does a *small* equilibrium constant ($K_{eq} \ll 1$) mean? It means that the reverse reaction is favored and that there will be more reactants than products when equilibrium is reached. For example, consider the following reaction.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \qquad K_{eq} = 4.1 \times 10^{-31} \text{ at } 25\,°C$$

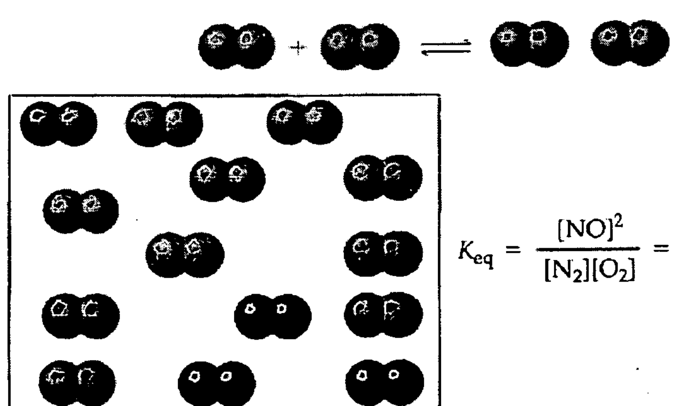
The equilibrium constant is very small, meaning that at equilibrium the reaction lies far to the left—high concentrations of reactants, low concentrations of products (▼ Figure 15.7). This is fortunate because N_2 and O_2 are the main components of air. If this equilibrium constant were large, much of the N_2 and O_2 in air would react to form NO, a toxic gas.

To summarize:

- $K_{eq} \ll 1$ Reverse reaction is favored; forward reaction does not proceed very far.
- $K_{eq} \approx 1$ Neither direction is favored; forward reaction proceeds about halfway.
- $K_{eq} \gg 1$ Forward reaction is favored; forward reaction proceeds virtually to completion.

The symbol $\approx$ means "approximately equal to."

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$



$$K_{eq} = \frac{[NO]^2}{[N_2][O_2]} = \text{Small Number}$$

▶ **Figure 15.7 The meaning of a small equilibrium constant** A small equilibrium constant means that there will be a high concentration of reactants and a low concentration of products at equilibrium.

15.5 Heterogeneous Equilibria: The Equilibrium Expression for Reactions Involving a Solid or a Liquid

Consider the following chemical reaction.

$$2\,CO(g) \rightleftharpoons CO_2(g) + C(s)$$

We might expect the expression for the equilibrium constant to be:

$$K_{eq} = \frac{[CO_2][C]}{[CO]^2} \quad \text{(incorrect)}$$

However, since carbon is a solid, its concentration is constant—it does not change. Adding more or less carbon to the reaction mixture does not change the concentration of carbon. The concentration of solids does not change because solids do not expand to fill their container. Their concentration, therefore, depends only on their density, which is constant as long as *some solid is present*. Consequently, pure solids—those reactants or products labeled in the chemical equation with an (*s*)—are not included in the equilibrium expression. The correct equilibrium expression is therefore:

The concentrations of pure solids and pure liquids are excluded from equilibrium expressions because they are constant. Consequently, they simply become incorporated into the value of the equilibrium constant.

$$K_{eq} = \frac{[CO_2]}{[CO]^2} \quad \text{(correct)}$$

Similarly, the concentration of a pure liquid does not change. Consequently, pure liquids—those reactants or products labeled in the chemical equation with an (*l*)—are also excluded from the equilibrium expression. For example, what is the equilibrium expression for the following reaction?

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Since $H_2O(l)$ is pure liquid, it is omitted from the equilibrium expression.

$$K_{eq} = \frac{[H^+][HCO_3^-]}{[CO_2]}$$

EXAMPLE 15.2 Writing Equilibrium Expressions for Reactions Involving a Solid or a Liquid

Write an equilibrium expression for the following chemical equation.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Solution:

Since $CaCO_3(s)$ and $CaO(s)$ are both solids, they are omitted from the equilibrium expression.

$$K_{eq} = [CO_2]$$

SKILLBUILDER 15.2 Writing Equilibrium Expressions for Reactions Involving a Solid or a Liquid

Write an equilibrium expression for the following chemical equation.

$$4\,HCl(g) + O_2(g) \rightleftharpoons 2\,H_2O(l) + 2\,Cl_2(g)$$

15.6 Calculating and Using Equilibrium Constants

Calculating Equilibrium Constants

The most direct way to get a value for the equilibrium constant of a reaction is to measure the concentrations of the reactants and products in a reaction mixture at equilibrium. For example, consider the following reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Equilibrium constants depend on temperature, so temperatures will often be included with equilibrium data. However, the temperature is not a part of the equilibrium expression.

Suppose a mixture of H_2 and I_2 is allowed to come to equilibrium at 445 °C. The measured equilibrium concentrations are $[H_2] = 0.11$ M, $[I_2] = 0.11$ M, and $[HI] = 0.78$ M. What is the value of the equilibrium constant? We begin by setting up the problem in the normal way.

Given:

$[H_2] = 0.11$ M
$[I_2] = 0.11$ M
$[HI] = 0.78$ M

Find: K_{eq}

Solution: The expression for K_{eq} can be written from the balanced equation.

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

To calculate the value of K_{eq}, simply substitute the correct equilibrium concentrations into the expression for K_{eq}.

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{[0.78]^2}{[0.11][0.11]} = 5.0 \times 10^1$$

The concentrations in an equilibrium expression should always be in units of molarity (M), but the units themselves are normally dropped.

The concentrations within K_{eq} must always be written in moles per liter (M); however, the units are normally dropped in expressing the equilibrium constant so that K_{eq} is unitless.

The particular concentrations of reactants and products for a reaction at equilibrium will *not* always be the same for a given reaction—they will depend on the initial concentrations. However, the *equilibrium constant* will always be the same at a given temperature, regardless of the initial concentrations. For example, Table 15.1 shows several different equilibrium concentrations of H_2, I_2, and HI, each from a different set of initial concentrations. Notice that the equilibrium constant is always the same, regardless of the initial concentrations. In other words, no matter what the initial concentrations are, the reaction will always go in a direction so that the equilibrium concentrations—when substituted into the equilibrium expression—give the same constant, K_{eq}.

A reaction can approach equilibrium from either direction, depending on the initial concentrations, but its K_{eq} at a given temperature will always be the same.

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TABLE 15.1 Initial and Equilibrium Concentrations for the Reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

Initial			Equilibrium			Equilibrium Constant
$[H_2]$	$[I_2]$	$[HI]$	$[H_2]$	$[I_2]$	$[HI]$	$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$
0.50	0.50	0.0	0.11	0.11	0.78	$\frac{[0.78]^2}{[0.11][0.11]} = 50$
0.0	0.0	0.50	0.055	0.055	0.39	$\frac{[0.39]^2}{[0.055][0.055]} = 50$
0.50	0.50	0.50	0.165	0.165	1.17	$\frac{[1.17]^2}{[0.165][0.165]} = 50$
1.0	0.5	0.0	0.53	0.033	0.934	$\frac{[0.934]^2}{[0.53][0.033]} = 50$

EXAMPLE 15.3 Calculating Equilibrium Constants

Consider the following reaction.

$$2\,CH_4(g) \rightleftharpoons C_2H_2(g) + 3\,H_2(g)$$

A mixture of CH_4, C_2H_2, and H_2 is allowed to come to equilibrium at 1700 °C. The measured equilibrium concentrations are $[CH_4] = 0.0203$ M, $[C_2H_2] = 0.0451$ M, and $[H_2] = 0.112$ M. What is the value of the equilibrium constant at this temperature?

Begin by setting up the problem in the normal format. You are given the concentrations of the reactants and products of a reaction at equilibrium. You are asked to find the equilibrium constant.

Given:

$$[CH_4] = 0.0203\text{ M}$$
$$[C_2H_2] = 0.0451\text{ M}$$
$$[H_2] = 0.112\text{ M}$$

Find: K_{eq}

Write the expression for K_{eq} from the balanced equation. To calculate the value of K_{eq}, simply substitute the correct equilibrium concentrations into the expression for K_{eq}.

Solution:

$$K_{eq} = \frac{[C_2H_2][H_2]^3}{[CH_4]^2}$$

$$K_{eq} = \frac{[0.0451][0.112]^3}{[0.0203]^2} = 0.154$$

SKILLBUILDER 15.3 Calculating Equilibrium Constants

Consider the following reaction.

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

A mixture of CO, H_2, and CH_3OH is allowed to come to equilibrium at 225 °C. The measured equilibrium concentrations are $[CO] = 0.489$ M, $[H_2] = 0.146$ M, and $[CH_3OH] = 0.151$ M. What is the value of the equilibrium constant at this temperature?

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Suppose that the preceding reaction is carried out at a different temperature and that the initial concentrations of the reactants are $[CO] = 0.500$ M and $[H_2] = 1.00$ M. Assuming that there is no product at the beginning of the reaction, and that at equilibrium $[CO] = 0.15$ M, find the equilibrium constant at this new temperature. Hint: Use the stoichiometric relationships from the balanced equation to find the equilibrium concentrations of H_2 and CH_3OH.

Using Equilibrium Constants in Calculations

The equilibrium constant can also be used to calculate the equilibrium concentration of one of the reactants or products, given the equilibrium concentrations of the others. For example, consider the following reaction.

$$2\,COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g) \qquad K_{eq} = 2.00 \text{ at } 1000\ ^\circ C$$

In an equilibrium mixture, the concentration of COF_2 is 0.255 M and the concentration of CF_4 is 0.118 M. What is the equilibrium concentration of CO_2? Again, we set up the problem in the normal way.

Given: $[COF_2] = 0.255$ M
$[CF_4] = 0.118$ M
$K_{eq} = 2.00$

Find: $[CO_2]$

Solution Map:

$$[COF_2],[CF_4],K_{eq} \longrightarrow [CO_2]$$

$$K_{eq} = \frac{[CO_2][CF_4]}{[COF_2]^2}$$

In this problem, we are given K_{eq} and the concentrations of one reactant and one product. We are asked to find the concentration of the other product. We can calculate this by using the expression for K_{eq}.

Solution: We first write the equilibrium expression for the reaction, and then solve it for the quantity we are trying to find ($[CO_2]$).

$$K_{eq} = \frac{[CO_2][CF_4]}{[COF_2]^2}$$

$$[CO_2] = K_{eq}\frac{[COF_2]^2}{[CF_4]}$$

Now simply substitute the appropriate values and compute $[CO_2]$.

$$[CO_2] = 2.00\frac{[0.255]^2}{[0.118]}$$
$$= 1.10 \text{ M}$$

EXAMPLE 15.4 Using Equilibrium Constants in Calculations

Consider the following reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \qquad K_{eq} = 69 \text{ at } 340\ ^\circ C$$

In an equilibrium mixture, the concentrations of H_2 and I_2 are both 0.020 M. What is the equilibrium concentration of HI?

You are given the equilibrium concentrations of the reactants in a chemical reaction and also given the value of the equilibrium constant. You are asked to find the concentration of the product.

Given:

$[H_2] = [I_2] = 0.020$ M
$K_{eq} = 69$

Find: [HI]

Draw a solution map showing how the equilibrium constant expression gives the relationship between the given concentrations and the concentration you are asked to find.

Solution Map:

$$[H_2],[I_2],K_{eq} \longrightarrow [HI]$$

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

Solve the equilibrium expression for [HI] and then substitute in the appropriate values to compute it.

Solution:

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

$$[HI]^2 = K_{eq}[H_2][I_2]$$

$$[HI] = \sqrt{K_{eq}[H_2][I_2]}$$

$$= \sqrt{69[0.020][0.020]}$$

$$= 0.17\ M$$

SKILLBUILDER 15.4 Using Equilibrium Constants in Calculations

Diatomic iodine (I_2) decomposes at high temperature to form I atoms according to the following reaction.

$$I_2(g) \rightleftharpoons 2\,I(g) \qquad K_{eq} = 0.011 \text{ at } 1200\ °C$$

In an equilibrium mixture, the concentration of I_2 is 0.10 M. What is the equilibrium concentration of I?

CONCEPTUAL CHECKPOINT 15.2

When the reaction $A(aq) \longrightarrow B(aq) + C(aq)$ is at equilibrium, each of the three compounds has a concentration of 2 M. The equilibrium constant for this reaction is:

(a) 4
(b) 2
(c) 1
(d) 1/2

15.7 Disturbing a Reaction at Equilibrium: Le Châtelier's Principle

Pronounced "le-sha-te-lyay."

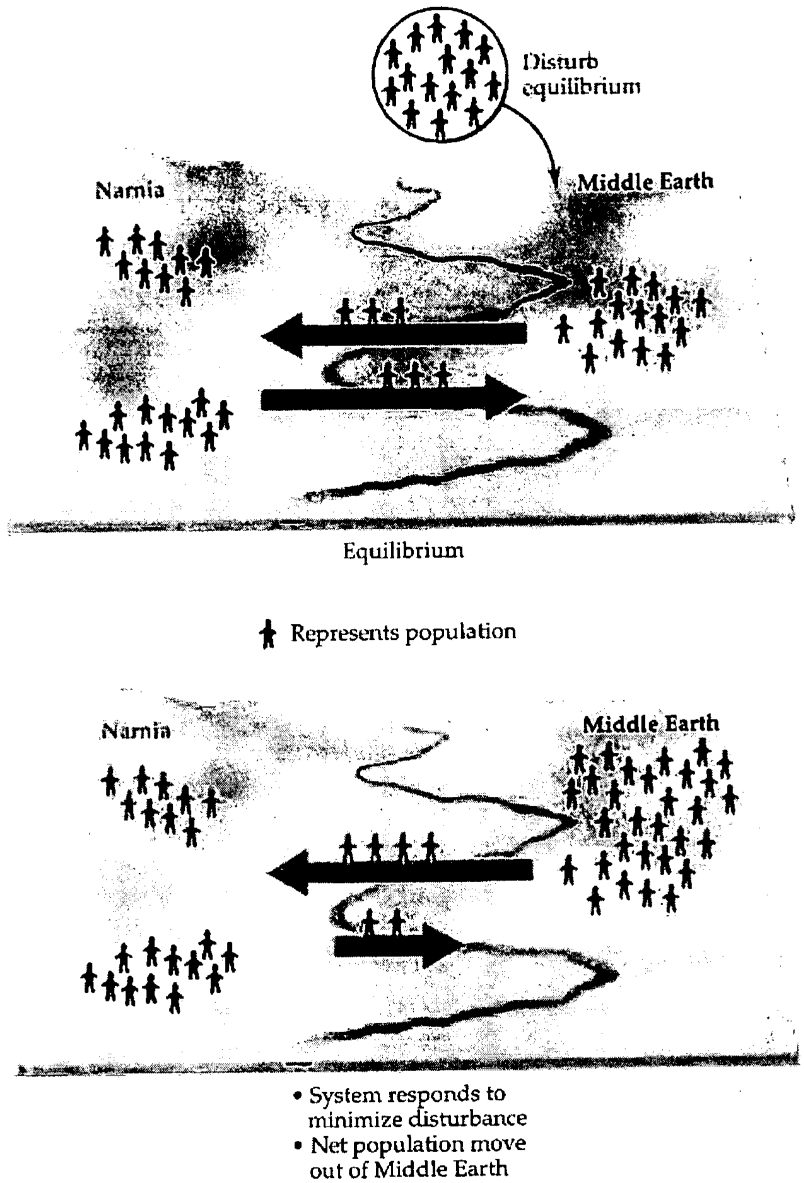
We have seen that a chemical system not in equilibrium tends to go toward equilibrium and that the concentrations of the reactants and products at equilibrium correspond to the equilibrium constant, K_{eq}. What happens, however, when a chemical system already at equilibrium is disturbed? **Le Châtelier's principle** states that the chemical system will respond to minimize the disturbance.

> **Le Châtelier's principle**—When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

In other words, a system at equilibrium tries to maintain that equilibrium—it fights back when disturbed.

We can understand Le Châtelier's principle by returning to our Narnia and Middle Earth analogy. Suppose the populations of Narnia and Middle Earth are at equilibrium. This means that the rate of people moving out of Narnia and into Middle Earth is equal to the rate of people moving into Narnia and out of Middle Earth, and the populations of the two kingdoms are

Figure 15.8 Population analogy for Le Châtelier's principle When a system at equilibrium is disturbed, it shifts to minimize the disturbance. In this case, adding population to Middle Earth (the disturbance) causes population to move out of Middle Earth (minimizing the disturbance.) Question: [illegible]



stable. Now imagine disturbing that balance (▲ Figure 15.8). Suppose we add extra people to Middle Earth. What happens? Since Middle Earth suddenly becomes more crowded, the rate of people leaving Middle Earth increases. The net flow of people is out of Middle Earth and into Narnia. Notice what happened. We disturbed the equilibrium by adding more people to Middle Earth. The system responded by moving people out of Middle Earth—it shifted in the direction that minimized the disturbance.

On the other hand, what happens if we add extra people to Narnia? Since Narnia suddenly gets more crowded, the rate of people leaving Narnia goes up. The net flow of people is out of Narnia and into Middle Earth. We added people to Narnia and the system responded by moving people out of Narnia. When systems at equilibrium are disturbed, they react to counter the disturbance. Chemical systems behave similarly. There are several ways to disturb a system in a chemical equilibrium. We consider each of these separately.

15.8 The Effect of a Concentration Change on Equilibrium

Consider the following reaction at chemical equilibrium.

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Suppose we disturb the equilibrium by adding NO_2 to the equilibrium mixture (▼ Figure 15.9). In other words, we increase the concentration of NO_2. What happens? According to Le Châtelier's principle, the system shifts in a direction to minimize the disturbance. The shift is caused by the increased concentration of NO_2 which in turn increases the rate of the reverse reaction because, as we covered in Section 15.2, reaction rates generally increase with increasing concentration. The reaction goes to the left (it proceeds in the reverse direction), consuming some of the added NO_2 and bringing its concentration back down.

When we say that a reaction *shifts to the left* we mean that it proceeds in the reverse direction, consuming products and forming reactants.

$$N_2O_4(g) \rightleftharpoons \underbrace{2\,NO_2(g)}_{\text{Add } NO_2}$$

$$\xleftarrow{\quad\quad}\ \text{Reaction shifts left}$$

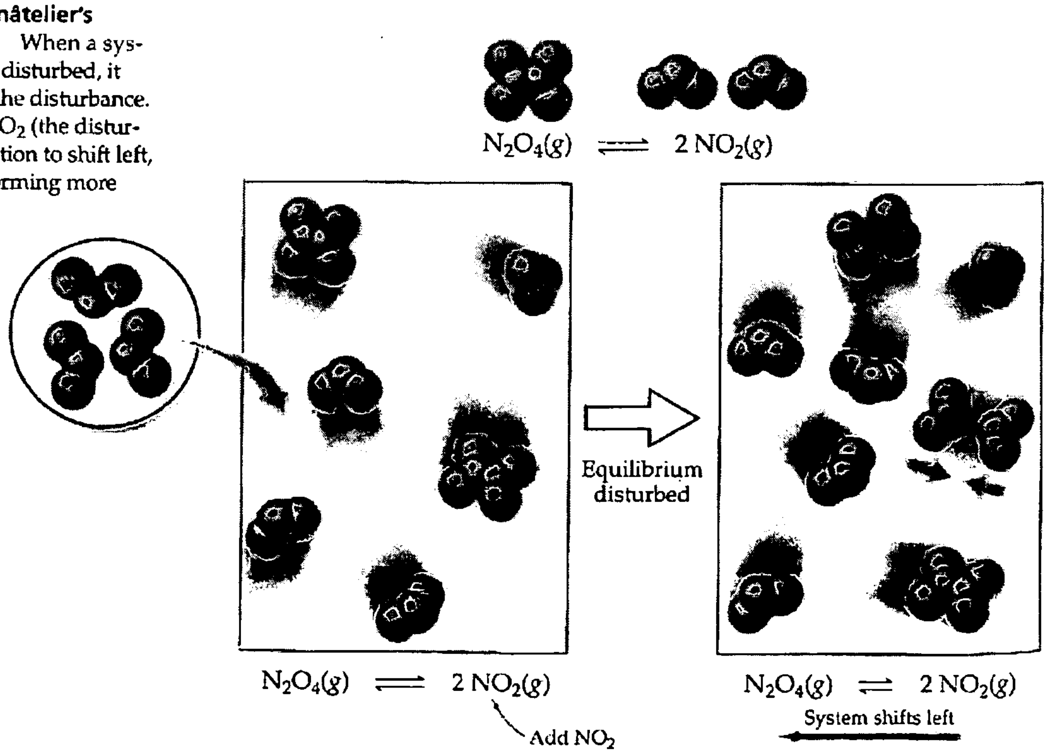
On the other hand, what happens if we add extra N_2O_4, increasing its concentration? In this case, the rate of the forward reaction increases and the reaction shifts to the right, consuming some of the added N_2O_4, and bringing *its* concentration back down (► Figure 15.10).

When we say that a reaction *shifts to the right* we mean that it proceeds in the forward direction, consuming reactants and forming products.

$$\underbrace{N_2O_4(g)}_{\text{Add } N_2O_4} \rightleftharpoons 2\,NO_2(g)$$

$$\text{Reaction shifts right}\ \xrightarrow{\quad\quad}$$

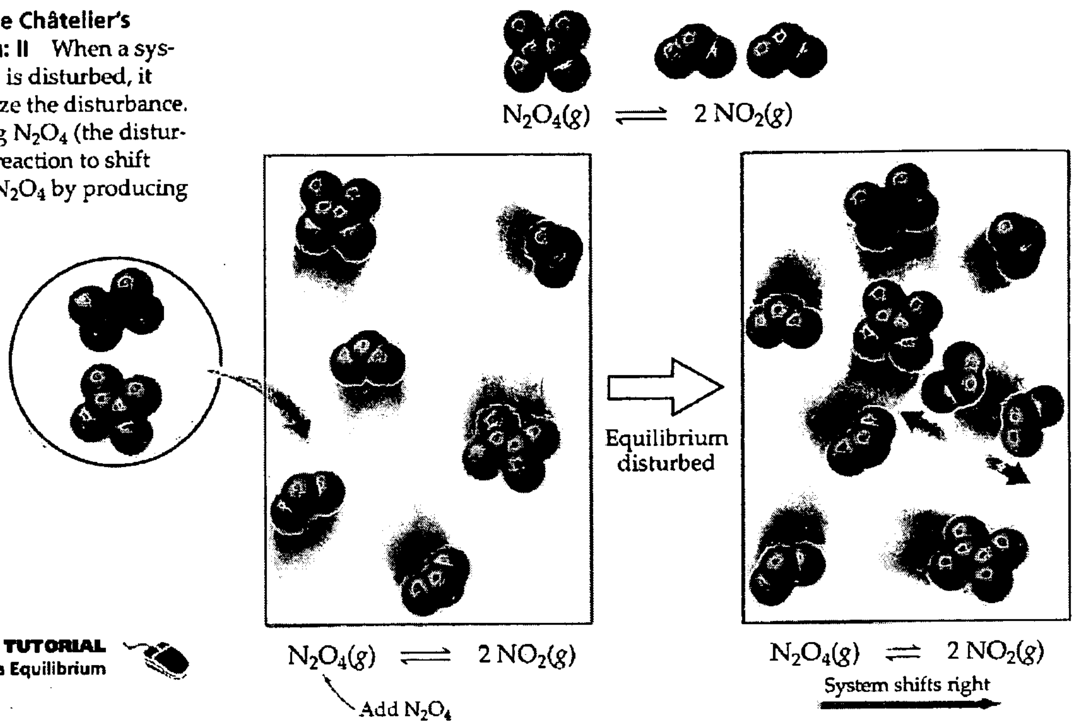
In both cases, the system shifts in a direction that minimizes the disturbance.



► **Figure 15.9 Le Châtelier's principle in action: I** When a system at equilibrium is disturbed, it changes to minimize the disturbance. In this case, adding NO_2 (the disturbance) causes the reaction to shift left, consuming NO_2 by forming more N_2O_4.

▶ **Figure 15.10 Le Châtelier's principle in action: II** When a system at equilibrium is disturbed, it changes to minimize the disturbance. In this case, adding N_2O_4 (the disturbance) causes the reaction to shift right, consuming N_2O_4 by producing more NO_2.

TUTORIAL
Ammonia Equilibrium



To summarize, if a chemical system is at equilibrium:

- Increasing the concentration of one or more of the reactants causes the reaction to shift to the right (in the direction of the products).
- Increasing the concentration of one or more of the products causes the reaction to shift to the left (in the direction of the reactants).

EXAMPLE 15.5 The Effect of a Concentration Change on Equilibrium

Consider the following reaction at equilibrium.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

What is the effect of adding additional CO_2 to the reaction mixture? What is the effect of adding additional $CaCO_3$?

Solution:

Adding additional CO_2 increases the concentration of CO_2 and causes the reaction to shift to the left. Adding additional $CaCO_3$ does not increase the concentration of $CaCO_3$ because $CaCO_3$ is a solid and thus has a constant concentration. It is therefore not included in the equilibrium expression and has no effect on the position of the equilibrium.

SKILLBUILDER 15.5 The Effect of a Concentration Change on Equilibrium

Consider the following reaction in chemical equilibrium.

$$2\,BrNO(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$$

What is the effect of adding additional Br_2 to the reaction mixture? What is the effect of adding additional BrNO?

SKILLBUILDER PLUS

What is the effect of removing some Br_2 from the preceding reaction mixture?

Chemistry AND HEALTH

How a Developing Fetus Gets Oxygen from Its Mother

Have you ever wondered how a baby in the womb gets oxygen? Unlike you and me, a fetus cannot breathe. Yet like you and me, a fetus needs oxygen. Where does that oxygen come from? In adults, oxygen is carried in the blood by a protein molecule called hemoglobin, which is abundantly present in red blood cells. Hemoglobin (Hb) reacts with oxygen according to the following equilibrium equation.

$$Hb + O_2 \rightleftharpoons HbO_2$$

The equilibrium constant for this reaction is neither large nor small, but intermediate. Consequently, the reaction can shift toward the right or the left, depending on the concentration of oxygen. As blood flows through the lungs, where oxygen concentrations are high, the equilibrium shifts to the right—hemoglobin loads oxygen.

Lung $[O_2]$ high

$$Hb + O_2 \rightleftharpoons HbO_2$$

Reaction shifts right

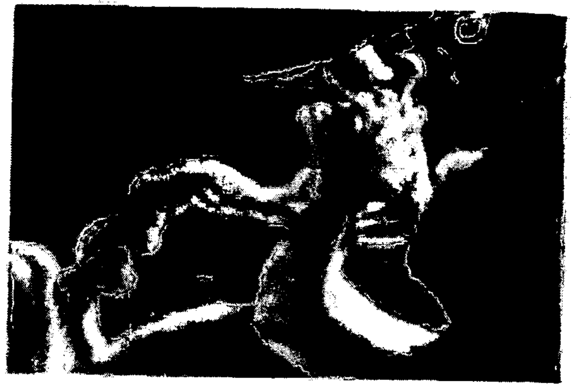
As blood flows through muscles and organs that are using oxygen (where oxygen concentrations have been depleted) the equilibrium shifts to the left—hemoglobin unloads oxygen.

Muscle $[O_2]$ low

$$Hb + O_2 \rightleftharpoons HbO_2$$

Reaction shifts left

However, a fetus has its own blood circulatory system. The mother's blood never flows into the fetus's body, and the fetus cannot get any air in the womb. So how does the fetus get oxygen?



▲ A human fetus. Question [illegible]

The answer lies in fetal hemoglobin (HbF), which is slightly different from adult hemoglobin. Like adult hemoglobin, fetal hemoglobin is in equilibrium with oxygen.

$$HbF + O_2 \rightleftharpoons HbFO_2$$

However, the equilibrium constant for fetal hemoglobin is larger than the equilibrium constant for adult hemoglobin. In other words, fetal hemoglobin will load oxygen at a lower oxygen concentration than adult hemoglobin. So, when the mother's hemoglobin flows through the placenta, it unloads oxygen into the placenta. The baby's blood also flows into the placenta, and even though the baby's blood never mixes with the mother's blood, the fetal hemoglobin within the baby's blood loads the oxygen (that the mother's hemoglobin unloaded) and carries it to the baby. Nature has thus engineered a chemical system where mother's hemoglobin can in effect *hand off* oxygen to the baby's hemoglobin.

CAN YOU ANSWER THIS? *What would happen if fetal hemoglobin had the same equilibrium constant for the reaction with oxygen as adult hemoglobin?*

15.9 The Effect of a Volume Change on Equilibrium

See Section 11.4 for a complete description of Boyle's law.

How does a system in chemical equilibrium respond to a volume change? Remember from Chapter 11 that changing the volume of a gas (or a gas mixture) results in a change in pressure. Remember also that pressure and volume are inversely related: a *decrease* in volume causes an *increase* in pressure, and an *increase* in volume causes a *decrease* in pressure. So, if the volume of a gaseous reaction mixture at chemical equilibrium is changed, the pressure changes and the system will shift in a direction to minimize that change. For example, consider the following reaction at equilibrium in a cylinder equipped with a moveable piston.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Notice that, from the ideal gas law ($PV = nRT$), we can see that lowering the number of moles of a gas (n) results in a lower pressure (P).

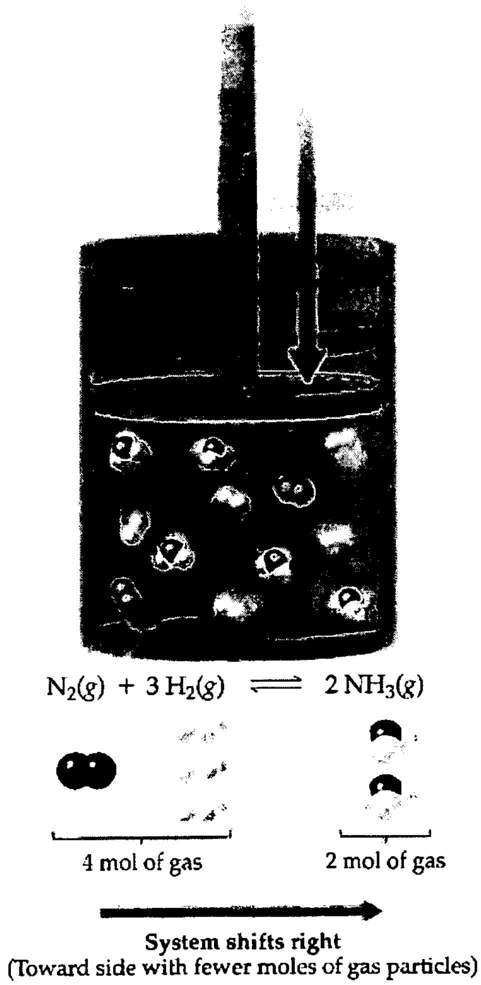
TUTORIAL
NO_2–N_2O_4
Equilibrium

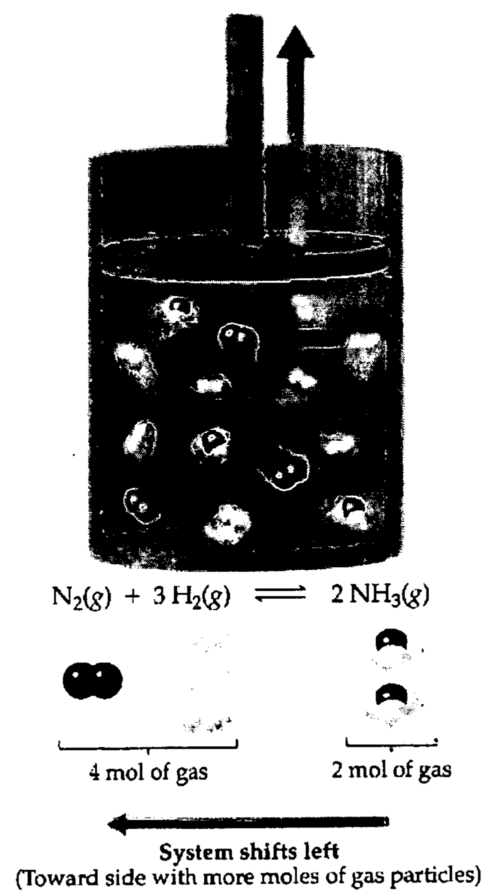
What happens if we push down on the piston, lowering the volume and raising the pressure (▼ Figure 15.11)? How can the chemical system bring the pressure back down? Look carefully at the reaction coefficients. If the reaction shifts to the right, 4 mol of gas particles are converted to 2 mol of gas particles. Fewer gas particles results in lower pressure. So the system shifts to the right, lowering the number of gas molecules and bringing the pressure back down, minimizing the disturbance.

Consider the same reaction mixture at equilibrium again. What happens if, this time, we pull *up* on the piston, *increasing* the volume (▼ Figure 15.12)? The higher volume results in a lower pressure and the system responds by trying to bring the pressure back up. It can do this by shifting to the left, converting 2 mol of gas particles into 4 mol of gas particles, increasing the pressure and minimizing the disturbance.

To summarize, if a chemical system is at equilibrium:

- Decreasing the volume causes the reaction to shift in the direction that has fewer moles of gas particles.
- Increasing the volume causes the reaction to shift in the direction that has more moles of gas particles.





▲ Figure 15.11 **Effect of volume decrease on equilibrium** When the volume of an equilibrium mixture is decreased, the pressure increases. The system responds (to bring the pressure back down) by shifting to the right, the side of the reaction with the fewest moles of gas particles.

▲ Figure 15.12 **Effect of volume increase on equilibrium** When the volume of an equilibrium mixture is increased, the pressure decreases. The system responds (to raise the pressure) by shifting to the left, the side of the reaction with the most moles of gas particles.

Notice that if a chemical reaction has an equal number of moles of gas particles on both sides of the chemical equation, a change in volume has no effect. For example, consider the following reaction.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Both the left and the right side of the equation contain 2 mol of gas particles, so a change in volume has no effect on this reaction. Similarly, a change in volume has no effect on a reaction that has no gaseous reactants or products.

EXAMPLE 15.6 | The Effect of a Volume Change on Equilibrium

Consider the following reaction at chemical equilibrium.

$$2\,KClO_3(s) \rightleftharpoons 2\,KCl(s) + 3\,O_2(g)$$

What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture?

Solution:

The chemical equation has 3 mol of gas on the right and 0 mol of gas on the left. Decreasing the volume of the reaction mixture increases the pressure and causes the reaction to shift to the left (toward the side with fewer moles of gas particles). Increasing the volume of the reaction mixture decreases the pressure and causes the reaction to shift to the right (toward the side with more moles of gas particles).

SKILLBUILDER 15.6 The Effect of a Volume Change on Equilibrium

Consider the following reaction at chemical equilibrium.

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture?

15.10 The Effect of a Temperature Change on Equilibrium

According to Le Châtelier's principle, if the temperature of a system at equilibrium is changed, the system should shift in a direction to counter that change. So if the temperature is increased, the reaction should shift in the direction that attempts to decrease the temperature and vice versa. Recall from Section 3.8 that energy changes are often associated with chemical reactions. If we want to predict the direction in which a reaction will shift upon a temperature change, we must understand how a shift in the reaction affects the temperature.

We can classify chemical reactions according to whether they absorb or emit heat energy in the course of the reaction. An **exothermic reaction** emits heat.

$$\text{Exothermic reaction} \qquad A + B \rightleftharpoons C + D + \text{Heat}$$

In an exothermic reaction, you can think of heat as a product. Consequently, raising the temperature of an exothermic reaction—think of this as adding heat—causes the reaction to shift left. For example, the reaction of nitrogen with hydrogen to form ammonia is exothermic.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3 + \text{Heat}$$

Reaction shifts left ← Add heat

Raising the temperature of an equilibrium mixture of these three gases causes the reaction to shift left, absorbing some of the added heat. Conversely, lowering the temperature of an equilibrium mixture of these three gases causes the reaction to shift right, releasing heat.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3 + \text{Heat}$$

Reaction shifts right → Remove heat

In contrast, an **endothermic reaction** absorbs heat.

$$\text{Endothermic reaction:} \quad A + B + \text{Heat} \rightleftharpoons C + D$$

TUTORIAL
Le Châtelier's Principle

In an endothermic reaction, you can think of heat as a reactant. Consequently, raising the temperature (or adding heat) causes an endothermic reaction to shift right. For example, the following reaction is endothermic.

$$\underset{\text{Colorless}}{N_2O_4(g)} + \text{Heat} \rightleftharpoons \underset{\text{Brown}}{2\,NO_2}$$

Add heat Reaction shifts right →

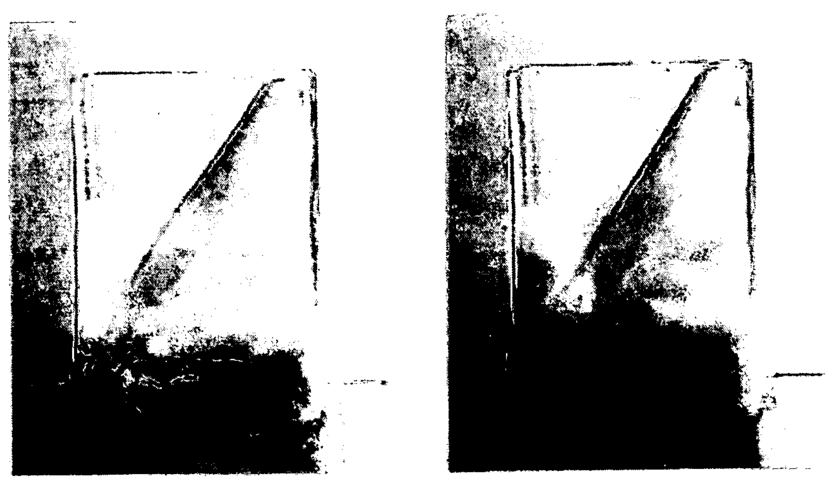
TUTORIAL
Nitrogen Dioxide and Dinitrogen Tetraoxide

Raising the temperature of an equilibrium mixture of these two gases causes the reaction to shift right, absorbing some of the added heat. Since N_2O_4 is colorless and NO_2 is brown, the effects of changing the temperature of this reaction are easily seen (▼ Figure 15.13). On the other hand, lowering the temperature of a reaction mixture of these two gases causes the reaction to shift left, releasing heat.

$$\underset{\text{Colorless}}{N_2O_4(g)} + \text{Heat} \rightleftharpoons \underset{\text{Brown}}{2\,NO_2}$$

Remove heat ← Reaction shifts left

▶ **Figure 15.13 Equilibrium as a function of temperature** Since the reaction $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ is endothermic, warm temperatures **(a)** cause a shift to the right, toward the production of brown NO_2. Cool temperatures **(b)** cause a shift to the left, to colorless N_2O_4.



(a) Warm: NO_2 **(b)** Cool: N_2O_4

To summarize:

In an exothermic chemical reaction, heat is a product and:

- Increasing the temperature causes the reaction to shift left (in the direction of the reactants).
- Decreasing the temperature causes the reaction to shift right (in the direction of the products).

In an endothermic chemical reaction, heat is a reactant and:

- Increasing the temperature causes the reaction to shift right (in the direction of the products).
- Decreasing the temperature causes the reaction to shift left (in the direction of the reactants).

EXAMPLE 15.7 The Effect of a Temperature Change on Equilibrium

The following reaction is endothermic.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?

Solution:

Since the reaction is endothermic, we can think of heat as a reactant.

$$\text{Heat} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Raising the temperature is adding heat, causing the reaction to shift to the right. Lowering the temperature is removing heat, causing the reaction to shift to the left.

SKILLBUILDER 15.7 The Effect of a Temperature Change on Equilibrium

The following reaction is exothermic.

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?

15.11 The Solubility-Product Constant

Recall from Section 7.7 that a compound is considered soluble if it dissolves in water and insoluble if it does not. Recall also that, through the *solubility rules* (Table 7.2), we classified ionic compounds as soluble or insoluble. We can better understand the solubility of an ionic compound with the concept of equilibrium. The process by which an ionic compound dissolves is an equilibrium process. For example, we can represent the dissolving of calcium fluoride in water with the following chemical equation.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

The equilibrium expression for a chemical equation that represents the dissolving of an ionic compound is called the **solubility-product constant** (K_{sp}). For CaF_2, the solubility-product constant is

$$K_{sp} = [Ca^{2+}][F^-]^2$$

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TABLE 15.2 Selected Solubility-Product Constants (K_{sp})

Compound	Formula	K_{sp}
barium sulfate	$BaSO_4$	1.07×10^{-10}
calcium carbonate	$CaCO_3$	4.96×10^{-9}
calcium fluoride	CaF_2	1.46×10^{-10}
calcium hydroxide	$Ca(OH)_2$	4.68×10^{-6}
calcium sulfate	$CaSO_4$	7.10×10^{-5}
copper(II) sulfide	CuS	1.27×10^{-36}
iron(II) carbonate	$FeCO_3$	3.07×10^{-11}
iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}
lead(II) chloride	$PbCl_2$	1.17×10^{-5}
lead(II) sulfate	$PbSO_4$	1.82×10^{-8}
lead(II) sulfide	PbS	9.04×10^{-29}
magnesium carbonate	$MgCO_3$	6.82×10^{-6}
magnesium hydroxide	$Mg(OH)_2$	2.06×10^{-13}
silver chloride	$AgCl$	1.77×10^{-10}
silver chromate	Ag_2CrO_4	1.12×10^{-12}
silver iodide	AgI	8.51×10^{-17}

Notice that, as we discussed in Section 15.5, solids are omitted from the equilibrium expression.

The K_{sp} value is an indicator of the solubility of a compound. A large K_{sp} (forward reaction favored) means that the compound is very soluble. A small K_{sp} (reverse reaction favored) means that the compound is not very soluble. Table 15.2 lists the value of K_{sp} for a number of ionic compounds.

EXAMPLE 15.8 Writing Expressions for K_{sp}

Write expressions for K_{sp} for each of the following ionic compounds.

(a) $BaSO_4$
(b) $Mn(OH)_2$
(c) Ag_2CrO_4

Solution:

To write the expression for K_{sp}, first write the chemical reaction showing the solid compound in equilibrium with its dissolved aqueous ions. Then write the equilibrium expression based on this equation.

(a) $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp} = [Ba^{2+}][SO_4^{2-}]$

(b) $Mn(OH)_2(s) \rightleftharpoons Mn^{2+}(aq) + 2\,OH^-(aq)$

$K_{sp} = [Mn^{2+}][OH^-]^2$

(c) $Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4^{2-}(aq)$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

SKILLBUILDER 15.8 Writing Expressions for K_{sp}

Write expressions for K_{sp} for each of the following ionic compounds.

(a) AgI
(b) $Ca(OH)_2$

Using K_{sp} to Determine Molar Solubility

Recall from Section 13.3 that the solubility of a compound is the amount of the compound that dissolves in a certain amount of liquid. The **molar solubility** is simply the solubility in units of moles per liter. The molar solubility of a compound can be computed directly from K_{sp}. For example, consider silver chloride:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) \qquad K_{sp} = 1.77 \times 10^{-10}$$

How can we find the molar solubility of AgCl from K_{sp}? First, notice that K_{sp} is *not* the molar solubility; it is the solubility-product constant.

Second, notice that the concentration of either Ag^+ or Cl^- at equilibrium will be equal to the amount of AgCl that dissolved. We know this from the relationship of the stoichiometric coefficients in the balanced equation.

$$1 \text{ mol AgCl} \equiv 1 \text{ mol } Ag^{+} \equiv 1 \text{ mol } Cl^{-}$$

Consequently, to find the solubility, we simply need to find $[Ag^+]$ or $[Cl^-]$ at equilibrium. We can do this by writing the expression for the solubility-product constant.

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

EVERYDAY Chemistry

Hard Water

Many parts of the United States obtain their water from lakes or reservoirs that have significant concentrations of $CaCO_3$ and $MgCO_3$. These salts dissolve into rainwater as it flows through soils rich in $CaCO_3$ and $MgCO_3$. Water containing these salts is known as hard water. Hard water is not a health hazard because both calcium and magnesium are part of a healthy diet, but their presence in water can be annoying. For example, because of their relatively low solubility-product constants, water can easily become saturated with $CaCO_3$ and $MgCO_3$. A drop of water, for example, becomes saturated with $CaCO_3$ and $MgCO_3$ as it evaporates. A saturated solution precipitates some of its dissolved ions. These precipitates show up as scaly deposits on faucets, sinks, or cookware. Washing cars or dishes with hard water leaves spots of $CaCO_3$ and $MgCO_3$ as these precipitate out of drying drops of water.

▲ Hard water leaves scaly deposits on plumbing fixtures.

CAN YOU ANSWER THIS? *Is the water in your community hard or soft? Use the solubility-product constants from Table 15.2 to calculate the molar solubility of $CaCO_3$ and $MgCO_3$. How many moles of $CaCO_3$ are in 5 L of water that is saturated with $CaCO_3$? How many grams?*

Since both Ag^+ and Cl^- come from AgCl, their concentrations must be equal. Since the concentration of either one is equal to the solubility, we can write:

$$\text{Solubility} = S = [Ag^+] = [Cl^-]$$

Substituting this into the expression for the solubility constant, we get:

$$\begin{aligned} K_{sp} &= [Ag^+][Cl^-] \\ &= S \times S \\ &= S^2 \end{aligned}$$

Therefore,

$$\begin{aligned} S &= \sqrt{K_{sp}} \\ &= \sqrt{1.77 \times 10^{-10}} \\ &= 1.33 \times 10^{-5}\ \text{M} \end{aligned}$$

So the molar solubility of AgCl is 1.33×10^{-5} mol/L.

In this text, we limit the calculation of molar solubility to ionic compounds whose chemical formulas have one cation and one anion.

EXAMPLE 15.9 Calculating Molar Solubility from K_{sp}

Calculate the molar solubility of $BaSO_4$.

Solution:

Begin by writing the reaction by which solid $BaSO_4$ dissolves into its constituent aqueous ions.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Next, write the expression for K_{sp}.

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

Define the molar solubility (S) as $[Ba^{2+}]$ or $[SO_4^{2-}]$ at equilibrium.

$$S = [Ba^{2+}] = [SO_4^{2-}]$$

Substitute S into the equilibrium expression and solve for it.

$$\begin{aligned} K_{sp} &= [Ba^{2+}][SO_4^{2-}] \\ &= S \times S \\ &= S^2 \end{aligned}$$

Therefore

$$S = \sqrt{K_{sp}}$$

Finally, look up the value of K_{sp} in Table 15.2 and compute S. The molar solubility of $BaSO_4$ is therefore 1.03×10^{-5} mol/L.

$$\begin{aligned} S &= \sqrt{K_{sp}} \\ &= \sqrt{1.07 \times 10^{-10}} \\ &= 1.03 \times 10^{-5}\ \text{M} \end{aligned}$$

SKILLBUILDER 15.9 Calculating Molar Solubility from K_{sp}

Calculate the molar solubility of $CaSO_4$.

15.12 The Path of a Reaction and the Effect of a Catalyst

In this chapter, we have learned that the equilibrium constant describes the ultimate fate of a chemical reaction. Large equilibrium constants mean that the reaction favors the products. Small equilibrium constants mean that the reaction favors the reactants. But the equilibrium constant by itself does not tell the whole story. For example, consider the following reaction between hydrogen gas and oxygen gas to form water.

Warning: Hydrogen gas is explosive and should never be handled without proper training.

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g) \qquad K_{eq} = 3.2 \times 10^{81} \text{ at } 25\ ^\circ C$$

The equilibrium constant is huge, meaning that the forward reaction is heavily favored. Yet I can mix hydrogen and oxygen in a balloon at room temperature, and no reaction occurs. Hydrogen and oxygen peacefully coexist together inside of the balloon and form virtually no water. Why?

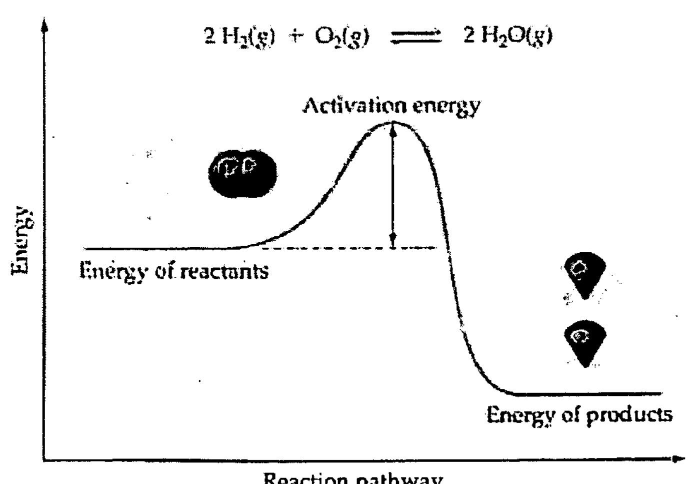
To answer this question, we must go back to a topic from the beginning of this chapter—the reaction rate. At 25 °C, the reaction rate between hydrogen gas and oxygen gas is virtually zero. Even though the equilibrium constant is large, the reaction rate is small and no reaction occurs. The reaction rate between hydrogen and oxygen is slow because the reaction has a large **activation energy:** energy that must be supplied in order to get a reaction started. Activation energies exist for most chemical reactions because the original bonds must begin to break before new bonds begin to form, and this requires energy. For example, for H_2 and O_2 to react to form H_2O, the H—H and O=O bonds must begin to break before the new bonds can form. The initial weakening of H_2 and O_2 bonds takes energy—this is the activation energy of the reaction.

The equilibrium constant describes *how far* a chemical reaction will go. The reaction rate describes *how fast* it will get there.

The activation energy is sometimes called the *activation barrier*.

How Activation Energies Affect Reaction Rates

We can illustrate how activation energies affect reaction rates by means of a graph showing the energy progress of a reaction (▼ Figure 15.14). We can see from the figure that the products have less energy than the reactants, so the reaction is exothermic (it releases energy when it occurs). However, before the reaction can take place, some energy must first be *added*—the energy of the reactants must be raised by an amount that we call the activation energy. The activation energy is thus a kind of "energy hump" that normally exists between the reactants and products.



▶ **Figure 15.14 Activation energy** This plot represents the energy of the reactants and products along the reaction pathway (as the reaction occurs). Notice that the energy of the products is lower than the energy of the reactants, so this is an exothermic reaction. However, notice that the reactants must get over an energy hump—called the *activation energy*—to proceed from reactants to products.

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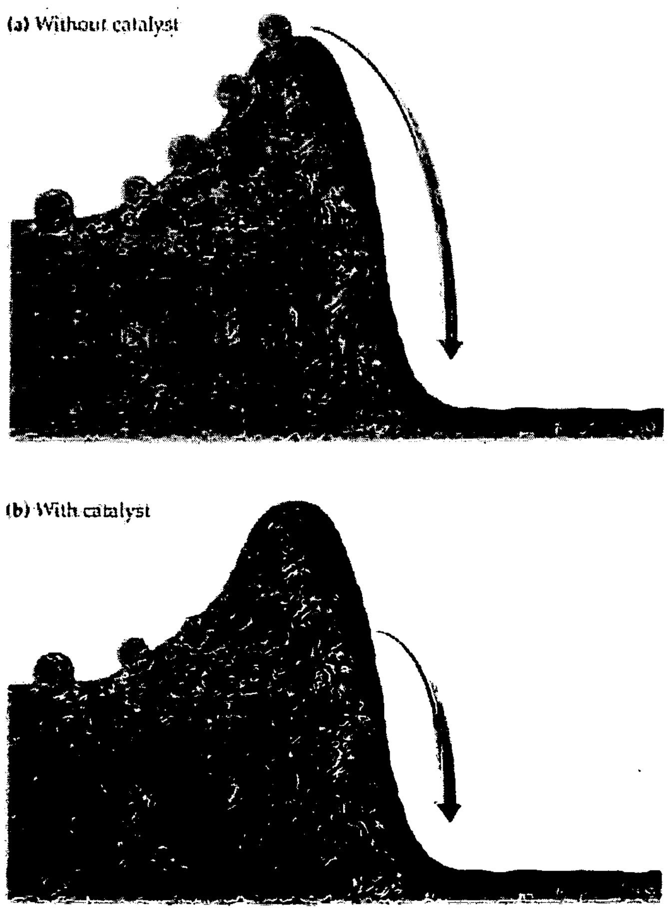
We can understand this concept better by means of a simple analogy—getting a chemical reaction to occur is much like trying to push a bunch of boulders over a hill (▼Figure 15.15a). We can think of each collision that occurs between reactant molecules as an attempt to roll a boulder over the hill. We can think of a successful collision between two molecules (one that leads to product) as a successful attempt to roll a boulder over the hill and down the other side.

For rolling boulders, the higher the hill is, the harder it will be to get the boulders over the hill, and the fewer the number of boulders that make it over the hill in a given period of time. Similarly, for chemical reactions, the higher the activation energy is, the fewer the number of reactant molecules that make it over the barrier, and the slower the reaction rate. In general:

> At a given temperature, the higher the activation energy for a chemical reaction, the slower the reaction rate.

Are there any ways to speed up a slow reaction (one with a high activation barrier)? In Section 15.2 we talked of two ways to increase reaction rates. The first way is to simply increase the concentrations of the reactants, which results in more collisions per unit time. This is analogous to simply pushing more boulders toward the hill in a given period of time. The second way to increase the rate of a reaction is to increase the temperature. This also results in more collisions per unit time, but it also results in collisions with higher energies. Higher-energy collisions are analogous to pushing the boulders harder (with more force), which will result in more boulders making it over the hill per unit time—a faster reaction rate. There is, however, a third way to speed up a slow chemical reaction: by using a *catalyst*.



▶ **Figure 15.15 Hill analogy for activation energy** There are several ways to get these boulders over the hill as fast as possible. **(a)** One way is simply to push them harder—this is analogous to an increase in temperature for a chemical reaction. **(b)** The other way is to find a path that goes *around* the hill—this is analogous to the role of a catalyst for a chemical reaction.

Catalysts Lower the Activation Energy

A catalyst does not change the *position* of equilibrium, only *how fast* equilibrium is reached.

A **catalyst** is a substance that increases the rate of a chemical reaction but is not consumed by the reaction. A catalyst works by lowering the activation energy for the reaction, making it easier for reactants to get over the energy hump (▼Figure 15.16). In our boulder analogy, a catalyst creates another path for the boulders to travel—a path with a smaller hill (see Figure 15.15b). For example, consider the noncatalytic destruction of ozone in the upper atmosphere.

$$O_3 + O \longrightarrow 2\,O_2$$

Upper-atmospheric ozone forms a shield against harmful ultraviolet light that would otherwise enter Earth's atmosphere. See the *Chemistry in the Environment* box in Chapter 6.

The reason that we have a protective ozone layer is that this reaction has a fairly high activation barrier and therefore proceeds at a fairly slow rate. The ozone layer does not rapidly decompose into O_2.

However, the addition of Cl (from synthetic chlorofluorocarbons) to the upper atmosphere has resulted in another pathway by which O_3 can be destroyed. The first step in this pathway—called the catalytic destruction of ozone—is the reaction of Cl with O_3 to form ClO and O_2.

$$Cl + O_3 \longrightarrow ClO + O_2$$

This is followed by a second step in which ClO reacts with O, regenerating Cl.

$$ClO + O \longrightarrow Cl + O_2$$

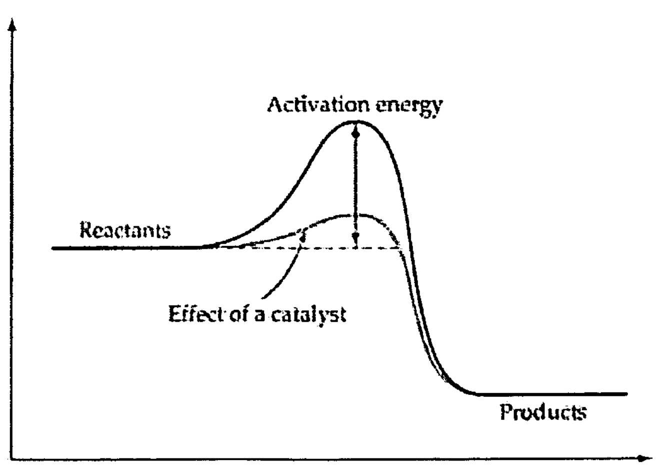
Notice that, if we add the two reactions, the overall reaction is identical to the noncatalytic reaction.

$$\begin{array}{l} \cancel{Cl} + O_3 \longrightarrow \cancel{ClO} + O_2 \\ \underline{\cancel{ClO} + O \longrightarrow \cancel{Cl} + O_2} \\ O_3 + O \longrightarrow 2\,O_2 \end{array}$$

However, the activation energies for the two reactions in this pathway are much smaller than for the first, uncatalyzed pathway, and therefore the reaction occurs at a much faster rate. Note that the Cl is not consumed in the overall reaction—this is characteristic of a catalyst.

In the case of the catalytic destruction of ozone, the catalyst speeds up a reaction that we do *not* want to happen. However, most of the time, catalysts are used to speed up reactions that we *do* want to happen. For example, your car most likely has a catalytic converter in its exhaust system. The catalytic converter contains a catalyst that converts exhaust pollutants (such as carbon monoxide) into less harmful substances (such as carbon dioxide). These reactions occur only with the help of a catalyst because they are too slow to occur otherwise.

▶ **Figure 15.16 Function of a catalyst** A catalyst provides an alternate pathway with a lower activation energy barrier for the reaction.



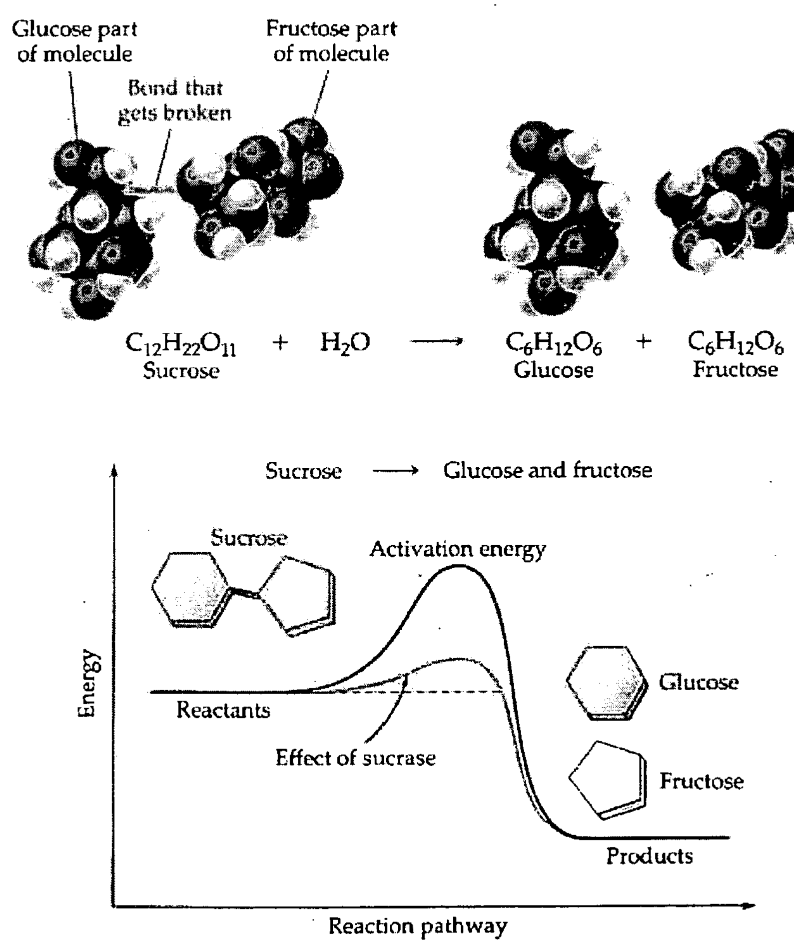
A catalyst cannot change the value of K_{eq} for a reaction—it affects only the rate of the reaction.

The role of catalysis in chemistry cannot be overstated. Without catalysts, chemistry would be a different field. For many reactions, increasing the reaction rate in other ways—such as increasing the temperature—are simply not feasible. Many reactants are thermally sensitive—increasing the temperature often destroys them. The only way to carry out many reactions is to use catalysts.

Enzymes: Biological Catalysts

Perhaps the best example of chemical catalysis is found in living organisms. Most of the thousands of reactions that must occur for a living organism to survive would be too slow at normal temperatures. So living organisms use **enzymes**, biological catalysts that increase the rates of biochemical reactions. For example, when we eat sucrose (table sugar), our bodies must break it into two smaller molecules called glucose and fructose. The equilibrium constant for this reaction is large, favoring the products. However, at room temperature, or even at body temperature, the sucrose does not break into glucose and fructose because the activation energy is high, resulting in a slow reaction rate. In other words, sugar remains sugar at room temperature even though the equilibrium constant for its reaction to glucose and fructose is high (▼Figure 15.17). In the body, an enzyme called *sucrase* catalyzes the conversion of sucrose to glucose and fructose. Sucrase has a pocket—called the active site—into which sucrose snugly fits (like a key into a lock). When sucrose is in the active site, the bond between the glucose and fructose units weakens, lowering the activation energy for the reaction

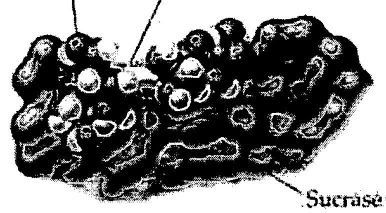
MOLECULE
Glucose



▲**Figure 15.17 An Enzyme catalyst** The enzyme sucrase creates a pathway with a lower activation energy for the conversion of sucrose to glucose and fructose.

and increasing the reaction rate (▼ Figure 15.18). The reaction can then proceed toward equilibrium—which favors the products—at a much lower temperature.

Not only do enzymes allow otherwise slow reactions to occur at a reasonable rate, they also allow living organisms to have tremendous control over which reactions occur, and when. Enzymes are extremely specific—each enzyme catalyzes only a single reaction. So if a living organism wants to turn a particular reaction on, it simply produces or activates the correct enzyme to catalyze that reaction.



► **Figure 15.18 How an enzyme works** Sucrase has a pocket called the active site where sucrose binds. When a molecule of sucrose enters the active site, the bond between glucose and fructose is weakened, lowering the activation energy for the reaction.

CHAPTER IN REVIEW

Chemical Principles	Relevance
The Concept of Equilibrium: Equilibrium involves the ideas of sameness and changelessness. When a system is in equilibrium, there is some property of the system that remains the same and does not change.	**The Concept of Equilibrium:** The equilibrium concept explains many phenomena such as the human body's oxygen delivery system. Life itself can be defined as controlled disequilibrium with the environment.
Rates of Chemical Reactions: The rate of a chemical reaction is the amount of reactant(s) that goes to product(s) in a given period of time. In general, reaction rates increase with increasing reactant concentration and increasing temperature. Since reaction rates depend on the concentration of reactants, and since the concentration of reactants decreases as a reaction proceeds, reaction rates usually slow down as a reaction proceeds.	**Rates of Chemical Reactions:** The rate of a chemical reaction determines how fast a reaction will reach its equilibrium. Chemists want to understand the factors that influence reaction rates so that they can control them.
Dynamic Chemical Equilibrium: Dynamic chemical equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.	**Dynamic Chemical Equilibrium:** When dynamic chemical equilibrium is reached, the concentrations of the reactants and products become constant.
The Equilibrium Constant: For the generic reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ the equilibrium constant (K_{eq}) is defined as: $K_{eq} = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$ Only the concentrations of gaseous or aqueous reactants and products are included in the equilibrium constant—the concentrations of solid or liquid reactants or products are omitted.	**The Equilibrium Constant:** The equilibrium constant is a measure of how far a reaction will proceed. A large K_{eq} means the forward reaction is favored (lots of products at equilibrium). A small K_{eq} means the reverse reaction is favored (lots of reactants at equilibrium). An intermediate K_{eq} means that there will be significant amounts of both reactants and products at equilibrium.

Le Châtelier's Principle: Le Châtelier's principle states that when a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

Effect of a Concentration Change on Equilibrium:

- Increasing the concentration of one or more of the *reactants* causes the reaction to shift to the *right*.
- Increasing the concentration of one or more of the products causes the reaction to shift to the *left*.

Effect of a Volume Change on Equilibrium:

- Decreasing the volume causes the reaction to shift in the direction that has *fewer* moles of gas particles.
- Increasing the volume causes the reaction to shift in the direction that has more moles of gas particles.

Effect of a Temperature Change on Equilibrium:
Exothermic chemical reaction (heat is a product):

- *Increasing* the temperature causes the reaction to shift *left*.
- *Decreasing* the temperature causes the reaction to shift *right*.

Endothermic chemical reaction (heat is a reactant):

- *Increasing* the temperature causes the reaction to shift *right*.
- *Decreasing* the temperature causes the reaction to shift *left*.

The Solubility-Product Constant, K_{sp}: The solubility-product constant of an ionic compound is the equilibrium constant for the chemical equation that describes the dissolving of the compound.

Reaction Paths and Catalysts: Most chemical reactions must overcome an energy hump, called the *activation energy*, as they proceed from reactants to products. Increasing the temperature of a reaction mixture increases the fraction of reactant molecules that make it over the energy hump, therefore increasing the rate. A catalyst—a substance that increases the rate of the reaction but is not consumed by it—lowers the activation energy so that it is easier to get over the energy hump *without* increasing the temperature.

Le Châtelier's Principle: Le Châtelier's principle helps us predict what happens to a chemical system at equilibrium when the conditions are changed. This allows chemists to modify the conditions of a chemical reaction to obtain a desired result.

Effect of a Concentration Change on Equilibrium: There are many cases when a chemist may want to drive a reaction in one direction or another. For example, suppose a chemist is carrying out a reaction to make a desired compound. The reaction can be pushed to the right by continuously removing the product from the reaction mixture as it forms, thus maximizing the amount of product that can be made.

Effect of a Volume Change on Equilibrium: Like the effect of concentration, the effect of pressure on equilibrium allows a chemist to choose the best conditions under which to carry out a chemical reaction. Some reactions are favored in the forward direction by high pressure (those with fewer moles of gas particles in the products) and others (those with fewer moles of gas particles in the reactants) are favored in the forward direction by low pressure.

Effect of a Temperature Change on Equilibrium: Again, the effect of temperature on a reaction allows chemists to choose conditions that will favor desired reactions. Higher temperatures favor endothermic reactions while lower temperatures favor exothermic reactions. Most reactions will occur *faster* at higher temperature, so the effect of temperature on the rate, not just on the equilibrium constant, must be considered.

The Solubility-Product Constant, K_{sp}: The solubility-product constant reflects the solubility of a compound. The greater the solubility-product constant, the greater the solubility of the compound.

Reaction Paths and Catalysts: Catalysts are used in many chemical reactions to increase the rates. Without catalysts, many reactions occur too slowly to be of any value. The thousands of reactions that occur in living organisms are controlled by biological catalysts called *enzymes*.